Polarized Luminescence and Chiroptical Switching Functionalities of Liquid Crystalline and Chiral Conjugated Polymers(Digest_要約)

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論文題目	Polarized Luminescence and Chiroptical Switching Functionalities of Liquid Crystalline and Chiral Conjugated Polymers （液晶性およびキラル共役系高分子の偏光発光とキラル光学スイッチング機能）		

（論文内容の要旨）

This research describes the synthesis and development of novel conjugated polymers exhibiting functionalities such as fluorescence, liquid crystallinity, and chirality. These functionalities enable advances in polarized luminescence and chiroptical switching leading to the development next-generation materials for applications in organic optoelectronics.

In **Part I**, the functional properties of *mono*-substituted polyacetylene (*mono*-PA) such as liquid crystallinity and chirality were tuned by controlling the feeding ratio of the *mono*-PA copolymers.

In **Chapter 1**, *mono*-PA copolymers consisting of a liquid crystalline acetylene monomer unit and an asymmetric center containing chiral acetylene monomer unit were synthesized. It is found from polarizing optical microscopy, X-ray diffraction, and circular dichroism (CD) spectra that the copolymers exhibited a smectic A (S_mA) phase and chirality, depending on the feeding ratio of the two monomers. The synthesized *mono*-PA copolymers could be potential photorefractive materials because of the electroclinic properties associated with the chiral smectic A (S_mA^*) phase.

In **Part II**, *di*-substituted liquid crystalline PA (*di*-LCPA) derivatives having fluorescence and liquid crystallinity were synthesized. The synthesized *di*-LCPAs were arranged linearly or helically to exhibit polarized functionalities such as linearly polarized luminescence (LPL) and circularly polarized luminescence (CPL).

In **Chapter 2**, the *di*-LCPA derivatives with liquid crystal (LC) moieties either directly attached or indirectly attached using flexible alkyl spacers to the main chain. The origin of emission of substituted PAs was elucidated by focusing on their substituents and structures. The thermotropic and lyotropic LC properties of the *di*-LCPAs and they were macroscopically aligned using rubbing technique were investigated. The aligned structures of the polymers are characterized through XRD measurements. The macroscopically aligned films of the polymers exhibit LPL with notable dichroic ratios. The electroluminescent (EL) devices using the polymers as the emissive polymer layer emit blue light with promising EL properties.

In **Chapter 3**, the *di*-LCPA derivatives with thermotropic and lyotropic LC behavior. The poly(diphenylacetylene) main chain structure of the *di*-LCPAs and the chirality induced by either chiral moieties or chiral dopants allow the formation of a highly ordered lyotropic chiral nematic liquid crystal (N*-LC) phase. The N*-LC state facilitates the formation of helically π-stacked structures with a high degree of helical ordering of the *di*-LCPA and is indispensable for the generation of CPL with high emission dissymmetry factors (g_{em}) on the order of 10^{-1}, the highest reported values of g_{em} for aliphatic conjugated polymers.

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In **Part III**, chiral conjugated polymers having helical structures in the aggregate states were synthesized. The synthesized chiral conjugated polymers exhibited novel chiral inversion in CD and CPL. Furthermore the dynamic switching of CPL by selective transmission through a N*-LC cell was elucidated.

Chapter 4 describes the synthesis of poly(*para*-phenyleneethynylene) (PPE) derivatives having two chiral moieties in both side chains and characterization of their solvent induced chiroptical properties. In varying ratios of chloroform and methanol solvents, the PPE aggregate exhibited a remarkable inversion of Cotton effects of CD and CPL. A facile way of chiral inversion of CPL in PPE through solvent induced aggregation and investigation of the nature of the helical structure present in the aggregate state was investigated.

In **Chapter 5**, poly(*para*-phenylene) (PPP) derivatives having photoresponsive chiral dithienylethene (DE*) end-groups were synthesized. In the assembled state, photoisomerization of the chiral DE* end-groups from open to closed form allowed a change in the handedness of the helical π-stacking structure. Furthermore, the chiral transcription of achiral poly(bithiophenethiophene) (PBTT) by chiral PPP in assembled state was demonstrated. The chirally transcribed PBTT showed helical inversion with the photoisomerization of the PPP chiral DE* end-groups.

Chapter 6 describes the dynamic switching of CPL in chiral *di*-LCPA from left- to right-handed CPL and vice-versa through the selective transmission of CPL across a thermotropic N*-LC phase. By combining a chiral *di*-LCPA CPL emitting film with a N*-LC cell and tuning the selective reflection band of the N*-LC phase to coincide with the CPL emission band, a CPL switchable cell were constructed. The phase change associated with the thermotropic N*-LC cell at varying temperatures allowed a change in selective transmission of CPL, enabling dynamic switching of CPL. The synergistic incorporation of chiral fluorescent conjugated polymers as CPL materials bearing the dynamic switching functionality of liquid crystals might lead to the emergence of next generation switchable low threshold lasers and optical memory devices.